Bio-butanol dehydration by zeolites: the missing link between classic and bio refinery

D. Gunst[1,2], K. Alexopoulos[2], A. Verberckmoes[1], M.F.-Reyniers[2]

[1]Industrial Catalysis and Adsorption Technology (INCAT), [2]Laboratory for Chemical Technology (LCT), Department of Chemical Engineering and Technical Chemistry, Ghent University

The commercial implementation of biofuel production is rapidly gaining interest due to its potential to create a more sustainable future [1]. This has led to an increasing commercial production of bio-butanol [2], which makes it an interesting and emerging bio-based building block in view of the depletion of fossil feedstocks. Utilizing these new bio-butanol feedstocks for the dehydration by zeolites, a *drop-in* approach via bio-butenes can be constructed towards existing refineries, which will facilitate commercialization and further upscaling. The use of zeolite catalysts, which have proven to be very versatile in usage within the classic refineries [3], will also further facilitate the implementation of these new processes.

To investigate the viability of the use of bio-butanol as a green chemical key molecule, the influence of the bio-butanol isomer and zeolite topology and the effects of temperature, site time and water content have been tested on the transformation towards butenes and higher hydrocarbons using a high-throughput reactor set-up. Comparing iso-butanol to 1-butanol in H-ZSM-5 shows an increase of activity from 20 mol% conversion to 60 mol% at identical conditions. Also iso-butene is being directly formed at high yields, above 50 %, at low temperatures of 503K when feeding iso-butanol. To gain more insights towards the changes of activity and selectivity of the iso-butanol feed, an in-depth theoretical analysis is performed with the help of ab-initio microkinetic simulations. Interestingly enough, a shift is observed in the dominant reaction path upon changing the reaction feed from 1-butanol to iso-butanol. Although 1-butanol dehydration proceeds predominantly via the ether-mediated path, the direct butene formation is favored in the case of iso-butanol dehydration.

This combined experimental and theoretical approach results in a very efficient way for the exploration of the different parameters, allowing to speed up the further development, upscaling and commercialization of these bio based products and processes [4].

[1] R. Luque, L. Herrero-Davila, J.M. Campelo, J.H. Clark, J.M. Hidalgo, D. Luna, J.M. Marinas, A.A. Romero, Energ Environ Sci. 1 (2008) 542-564.
[2] C. Jin, M.F. Yao, H.F. Liu, C.F.F. Lee, J. Ji, Renew Sust Energ Rev. 15 (2011) 4080-4106.
[3] T.F. Degnan, J Catal. 216 (2003) 32-46.
[4] M. John, K. Alexopoulos, M.-F. Reyniers, G. B. Marin, J Catal. 330 (2015) 28-45.

E-mail: dieter.gunst@Ugent.be